

What is claimed is:

1 1. A layered proton exchange membrane, comprising:
2 an organic/inorganic composite membrane, comprising
3 inorganic proton conductor and organic base
4 polymer; and
5 at least one proton exchange membrane.

1 2. The layered proton exchange membrane as claimed
2 in claim 1, wherein the inorganic proton conductor is H₃O⁺
3 β-alumina, Sb₂O₅*5.4H₂O, H-modenite, heteropoly acid,
4 zeolite, zirconium phosphate, silicon oxide, titanium
5 oxide, tungsten acid, sulfated zirconia, sulfated
6 alumina, sulfated titanium oxide or sulfated titanium-
7 aluminum oxide.

1 3. The layered proton exchange membrane as claimed
2 in claim 1, wherein the organic base polymer is a proton
3 conductive polymer.

1 4. The layered proton exchange membrane as claimed
2 in claim 1, wherein the organic base polymer and base
3 material of the proton exchange membrane are polymers
4 with cationic ion exchange groups.

1 5. The layered proton exchange membrane as claimed
2 in claim 4, wherein the polymers with cationic ion
3 exchange groups are poly(vinylidenefluoride)-grafted-
4 sulfonatedpolystyrene (PVDF-g-SPS), PVDF-g-sulfonated-
5 poly(N-vinylcarbazole), PVDF-g-poly(vinylphosphonic
6 acid), PVDF-g-poly(4-vinylbenoic acid), PVDF-g-

7 Sulfonated-poly(2-vinylnaphthalene), or PVDF-g-
8 Sulfonated-poly(9-vinylanthracene).
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1 6. The layered proton exchange membrane as claimed
2 in claim 5, wherein the cationic ion exchange resins are
3 sulfonate, carboxylate, phosphonate, imide, sulfonimide
4 or sulfonamide.

1 7. The layered proton exchange membrane as claimed
2 in claim 1, wherein the organic base polymer further
3 comprises fluorine-containing resin to form the
4 organic/inorganic composite membrane.

1 8. The layered proton exchange membrane as claimed
2 in claim 7, wherein the fluorine-containing resin is
3 poly(vinylidenefluoride), poly(vinylidenefluoride/
4 hexafluoropropylene) copolymer, poly(vinylidenefluoride/
5 chlorotrifluoroethylene)copolymer,
6 poly(vinylidenefluoride/hexafluoropropylene/tetrafluoro
7 ethylene) tripolymer or poly(chlorotrifluoro ethylene).

1 9. The layered proton exchange membrane as claimed
2 in claim 1, wherein the organic base polymer further
3 comprises non fluorine-containing resin to form the
4 organic/inorganic composite membrane.

1 10. The layered proton exchange membrane as claimed
2 in claim 9, wherein the non fluorine-containing resin is
3 polyacrylate, polyester, polyetherketone, polysulfone,
4 polyether, polyamide, polyphenylene oxide or polyethylene
5 oxide.

1 11. The layered proton exchange membrane as claimed
2 in claim 1, wherein the methanol permeability of the
3 organic/inorganic composite membrane is less than $10^{-7}\text{cm}^2/\text{s}$.
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1 12. The layered proton exchange membrane as claimed
2 in claim 1, wherein the proton conductivity of the
3 organic/organic composite membrane is at least 10^{-4}S/cm .

1 13. A method for preparing a layered proton exchange
2 membrane, comprising of:

3 (a) forming an organic/inorganic composite membrane
4 by doping inorganic proton conductor in organic
5 base polymer; and

6 (b) combining the organic/inorganic complex membrane
7 and a proton exchange membrane to form a
8 layered proton exchange membrane.

1 14. The method as claimed in claim 13, wherein the
2 step (a) is performed by physical blending, chemical
3 cross-linking, UV radiation cross-linking or sol-gel.

1 15. The method as claimed in claim 13, wherein the
2 step (b) is performed by thermal pressing, chemical
3 cross-linking or UV radiation cross-linking.

1 16. The method as claimed in claim 13, wherein the
2 number of the proton exchange membrane is at least one
3 and the organic/inorganic composite membrane is located
4 on one side of the layered proton exchange membrane.

1 17. The method as claimed in claim 13, wherein step
2 (b) further comprises combining an adhesive film between
3 the organic/inorganic composite membrane and the proton
4 exchange membrane.

1 18. The method as claimed in claim 13, further
2 comprising introducing cationic ion exchange groups into
3 the layered proton exchange membrane.

1 19. A direct liquid-feed methanol fuel cell,
2 comprising:

3 a cathode;

4 an anode; and

5 a layered proton exchange membrane, formed by
6 lamination of an organic/inorganic composite
7 membrane with at least one proton exchange
8 membrane, wherein the organic/inorganic
9 composite membrane comprises organic base
10 polymer and inorganic proton conductor.

1 20. The direct methanol fuel cell as claimed in
2 claim 19, wherein the methanol permeability of the
3 organic/inorganic composite membrane is less than $10^{-7} \text{ cm}^2/\text{s}$.

1 21. The direct methanol fuel cell as claimed in
2 claim 19, wherein the proton conductivity of the
3 organic/inorganic composite membrane is at least 10^{-4} S/cm .